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DETERMINATION OF MOLECULAR HYDROGEN SULFIDE

Thomas B. Hoover

National Environmental Research Center

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DETERMINATION OF MOLECULAR HYDROGEN SULFIDE

by

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The gas sparging technique and a new gas-sensing electrode were evaluated for the determination of dissolved molecular hydrogen sulfide at environmentally significant concentrations in water. From the sparging experiments approximate coefficients were obtained for the distribution of hydrogen sulfide between nitrogen and distilled water, seawater, or municipal sewage effluent. In the latter medium the volatility of hydrogen sulfide was very much less than predicted from the pH-total sulfide relationship. The electrode, consisting of various semipermeable membranes, buffered electrolyte filling solution, silver-silver sulfide crystal sensor, and lanthanum fluoride internal reference electrode, gave a generally Nernstian response to more than 0.1 mg/l of molecular hydrogen sulfide. At lower concentrations the response was typically several tenths of a volt per decade of concentration, but was not reproducible among different samples or electrodes. Various sources of the anomalous behavior were considered. The electrode is recommended for in situ measurements of molecular hydrogen sulfide at concentrations greater than 0.1 mg/l. More work is needed to make it useful at lower concentrations.

This report was submitted in fulfillment of ROAP 16ADN, Task 38 by the Southeast Environmental Research Laboratorh, Athens, Georgia, under the sponsorship of the Environmental Protection Agency. Work was completed as of March 1974.

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Most of the experimental work was performed by Mr. George D. Yager.

SECTION I

CONCLUSIONS

A new, gas-sensing electrode responded logarithmically to molecular hydrogen sulfide in water at concentrations greater than 0.1 mg/l.

At hydrogen sulfide concentrations significantly less than 0.1 mg/l the electrode usually gave an anomalous response of several hundred millivolts per decade of concentration.

The same quantitative performance was obtained with a variety of membranes and filling solutions.

Both the electrode and gas sparging techniques measured the thermodynamic activity of hydrogen sulfide, which is a function of the ionic strength of the solution. In seawater the activity was approximately 20% greater than the stoichiometric concentration of the molecular species.

In sewage effluent the indicated concentration of molecular hydrogen sulfide was very much less than the value calculated from the ionization constant, pH, and total sulfide concentration, as added or determined by the methylene blue method.

SECTION II

RECOMMENDATIONS

The gas-sensing hydrogen sulfide electrode is recommended for applications where the molecular species of hydrogen sulfide in water must be measured directly, *in situ*, at concentrations greater than 0.1 mg/l.

The wide millivolt range of the gas electrode and good repeatability of response, at least for a particular electrode and sample, suggest that the device might be useful at very much lower levels of hydrogen sulfide if the response were more predictable. The non-Nernstian behavior at low concentrations of hydrogen sulfide may be related both to thin film liquid diffusion and to interfacial potential mechanisms. The kinetics and mechanism of the silver sulfide solid-state sensor response should be studied as a function of surface treatment and condition of the crystal sensor.

SECTION III

INTRODUCTION

Sulfides frequently occur at environmentally harmful levels in the hypolimnion of lakes and fiords as a result of anoxic decomposition of organic matter, and may also result from industrial pollution. Evidence (1,2) indicates that the toxicity to fish of dissolved molecular species of hydrogen sulfide is greater than that of the ionic species in equilibrium with it. To assess the ecological significance of dissolved sulfides more accurately a direct analytical method is needed for the molecular species in the approximate concentration range of 10 µg/l to 3 mg/l.

The calculation of un-ionized hydrogen sulfide from total sulfide and pH (3) requires corrections for temperature and ionic strength. A method based on gas sparging of the molecular species from a water sample, followed by colorimetric determination of the total sulfide removed, was developed under contract (4). The present report deals with an evaluation of the sparge method, especially as applied to polluted and saline samples, and a study of a new "gas-sensing" electrode technique for determining molecular hydrogen sulfide in water.

SECTION IV

GAS SPARGING

REQUIREMENTS AND LIMITATIONS

Although gas sparging is, in principle, a relatively straight-forward means of determining a gaseous species in solution, it has some severe limitations. For the amount of substance determined in the gas stream to bear a direct relation to the concentration in the solution, it is important that the solution not be altered appreciably by the sparging process. In a well buffered solution of high total sulfide content and high pH the amount of H_2S removed may be many times that actually present as the neutral species in the solution at any instant without displacing the equilibrium significantly, since the reservoir of sulfide ion can maintain steady conditions. On the other hand, in an unbuffered solution of low total sulfide concentration the removal of even 10% of the neutral species can alter the equilibrium appreciably. The latter situation is more typical of the natural waters of interest. Therefore, the sparging process must be restricted to removing a small fraction of the species in the sample. A very sensitive analytical technique is then required.

In addition, the sparge technique is ill-adapted to field use, and the transportation of samples to a laboratory imposes problems of sampling, storage, and preservation of a component that is volatile, subject to oxidation, and in labile equilibrium with ionic forms. Consequently, there may be serious difficulties in relating the laboratory determination to actual conditions in the field.

Use of the sparge technique involves the assumption that the ionic activity coefficients and the distribution coefficient of hydrogen sulfide between the sample and the sparge gas are constant from sample to sample, or can be estimated with sufficient precision.

ROCKETDYNE RESULTS

In the contract work at Rocketdyne (4) samples were sparged with nitrogen and the removed H_2S was trapped as CdS and determined by the methylene blue colorimetric procedure. With the use of 10-cm path-length microcells, a photometric detection limit of 0.2 µg H_2S was obtained. The determination of H_2S at a concentration of 1 µg/l, while removing no more than 10% of the H_2S in the sample, therefore required a sample of at least two liters. Most

calibrations were made in 0.01 M solutions of Na_2S in deionized water or in 3.5% NaCl. Calculated molecular H_2S concentrations were 3 - 34 µg/l. Observed methylene blue absorbances were compared with absorbances calculated assuming ideal extraction and constant molar absorption coefficient. On this basis, recoveries were 85-100%, with relative standard deviations of 2-5%. Only two runs simulated natural conditions, with low total sulfide (3 µg/l, essentially all in the molecular form); 85% recoveries were obtained in each run. Because of the high recoveries and agreement between runs in deionized water and in 3.5% salt solution the contractor concluded that the method was applicable to freshwater and seawater without making ionic strength corrections.

EXPERIMENTAL

Some in-house tests of the sparge method were made to check its applicability to several natural samples with the objective of using it as a referee method for checking the gas-sensing electrode. The apparatus, shown in Figure 1, included a sparge chamber of a design essentially the same as that used by Rocketdyne (4), but with a liquid capacity of one liter, as compared to the two-liter capacity of the Rocketdyne chamber. Hydrogen sulfide was trapped by passing the sparge gas through 5 ml of 0.02 N NaOH above a fine sintered glass disk. Negligible sulfide was collected in a second similar trap in series, demonstrating the efficiency of collection. The volume of sparge gas was measured by displacement rather than by flow rate. The methylene blue determination was made by the procedure of Reference 4, using 1-cm cells in a Beckman Model B spectrophotometer at 670 nm. The detection limit was about 1 µg of H_2S and the apparent molar absorbance based on the calibration curve between 1×10^{-4} M and 2.5×10^{-5} M sulfide was 25×10^3. The test solution was sampled at intervals from the bottom of the sparge column to provide a material balance and determination of the distribution coefficient.

The initial sulfur concentration in the sample (S_T, mol/l) was calculated using the total amount of sulfur in the sample and in the trap after sparging. Analytical concentrations in the sample and trap were determined from the spectrophotometer readings and calibration curve, with allowance for dilution of the specimen taken for analysis. The activity of sulfide ion species, S^{2-} in the sample was calculated according to Equation 1, using S_T and the measured pH.

$$[S^{2-}] = S_T/[(10^{-2pH}/K_1K_2) + (10^{-pH}/\gamma_1K_2) + (1/\gamma_2)] \qquad (1)$$

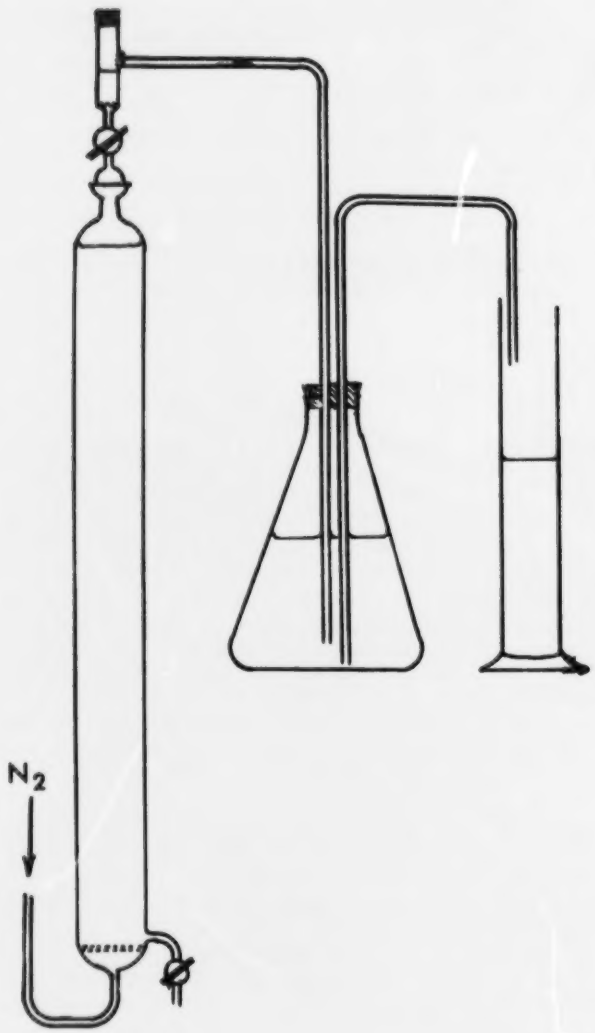

FIGURE 1. Gas-Sparging Apparatus

K_1 and K_2 are the respective ionization constants for hydrogen sulfide, taking pK_1 = 7.02 (5) and pK_2 = 13.78 (6). The activity coefficients of the singly- and doubly-charged ions, γ_1 and γ_2, respectively, were estimated from a graph provided by Orion Research (7) for simple electrolyte solutions having ionic strengths less than 1 M. In seawater, γ_1 and γ_2 were taken as 0.68 and 0.16, respectively (8). In sewage effluent, 0.95 and 0.90 were used arbitrarily for γ_1 and γ_2. The negative logarithm of the activity of the molecular species of hydrogen sulfide was calculated from ionization constants by Equation 2.

$$pH_2S = 2\ pH + pS^{2-} - pK_1 - pK_2 \qquad (2)$$

The apparent distribution coefficient, P_D, was obtained by dividing the molar concentration of molecular hydrogen sulfide in the water by the molar concentration in the sparge gas. The latter was obtained by dividing the moles of sulfide collected in the trap by the corresponding number of liters of nitrogen used. The concentration in the water was the mean value calculated for samples taken at the beginning and end of the sparge period. The material balance, expressed on a percentage basis, was obtained by dividing the total number of moles of sulfide initially in the water into the sum of the moles of sulfide in the water at the end of the run, that collected in the trap, and that in water samples taken for analysis.

The results of several sparge runs are summarized in Table 1. In all but one run, 1.5 l of nitrogen was used and two or more intermediate samples were withdrawn. No more than one fourth of the total sulfide in the sample was removed as sparged hydrogen sulfide during a run and generally less than ten percent was removed between successive analyses. Material balances on total sulfur were between 80 and 120%.

The results are best compared in terms of the derived distribution coefficient for hydrogen sulfide between the aqueous solution and nitrogen. The mean value of the distribution coefficient obtained from five runs in de-ionized water was 2.18, with a standard deviation of 0.43. In reference 4, consistent recoveries were obtained on the basis of a distribution coefficient of 2.50, which was obtained from solubility measurements at very much higher concentrations of hydrogen sulfide (9). For three runs in seawater we found a mean value for P_D of 1.79, with a standard deviation of 0.24. A value lower than that in

Table 1. GAS SPARGING OF HYDROGEN SULFIDE

Run	Sparge Vol. (ℓ)	pH	S_{TOT} $\underline{M}x10^5$	H_2S $\underline{M}x10^5$	Collected H_2S (μmoles)	Distribution Coeff.	Mat'l. Bal.
1. Deionized Water 1.14 ppm H_2S	0	7.59	16.4	2.11	3.70	2.90	98.7%
	0.5	7.65	16.2	1.87	2.88		
	1.0	7.70	15.1	1.56	2.45		
	1.5	7.76	15.2	1.41			
2. Deionized Water 2.69 ppm H_2S	0	6.58	11.0	5.00	12.75	1.74	113.4%
	0.5	6.64	10.8	4.73	13.50		
	1.0	6.74	9.8	3.99	10.62		
	1.5	6.84	8.7	3.24			
3. Deionized Water 2.12 ppm H_2S	0	6.89	11.1	3.94	8.17	2.05	99.1%
	0.5	6.94	9.3	3.11	7.75		
	1.0	7.02	9.2	2.82	6.46		
	1.5	7.06	8.7	2.54			
4. Deionized Water 2.53 ppm H_2S	0	6.93	13.8	4.70	9.67	2.08	97.2%
	0.5	7.00	12.1	3.81	8.96		
	1.0	7.07	10.5	3.02	6.88		
	1.5	7.15	10.8	2.84			
5. Deionized Water 1.75 ppm H_2S	0	6.96	9.9	3.26	24.6	2.15	110.1%
	2.0	7.12	8.4	2.16			
6. Seawater 1.03 ppm H_2S	0	6.85	9.8	3.04	6.92	1.79	91.6%
	0.5	7.09	9.4	2.11	5.46		
	1.0	7.23	7.4	1.34	2.88		
	1.5	7.41	7.3	0.89			

Table 1 (continued). GAS SPARGING OF HYDROGEN SULFIDE

Run	Sparge Vol. (ℓ)	pH	S_{TOT} $\underline{M}x10^5$	H_2S $\underline{M}x10^5$	Collected H_2S(μmoles)	Distribution Coeff.	Mat'l. Bal.
7. Seawater	0	6.45	9.85	3.97			
	0.3				7.03		
1.35 ppm H_2S	.6	6.70	9.90	3.10	6.18		
	.9				5.38	1.55	117.8%
	1.2	6.93	9.10	2.12	5.00		
	1.5	7.13	8.90	1.56	3.70		
8. Seawater	0	7.36	20.6	1.88	2.42		
	0.3				2.49		
0.64 ppm H_2S	.6	7.52	15.0	1.36	1.85	2.04	79.6%
	.9	7.60	15.2	1.16	1.76		
	1.2				1.51		
	1.5	7.64	15.0	1.08			
9. Sewage	0	6.45	450	219			
Effluent	0.5	6.67	510	216	1.30		
74.5 ppm H_2S	1.0	6.73	540	217	1.25	777	107.8%
	1.5	6.79	482	184	1.20		
10. Sewage	0	6.74	830	331			
Effluent	0.5	6.84	750	274	2.97		
	1.0	6.94	750	246	2.60	475	88.4%
112.5 ppm H_2S	1.5	7.03	725	215	2.76		

deionized water is expected since neutral molecules are generally salted out of the high ionic strength seawater. The activity coefficient of neutral ion pairs in seawater has been estimated as 1.13 at 25° C. The ratio of the measured distribution coefficients (2.18/1.79) corresponds to an activity coefficient for molecular hydrogen sulfide in seawater of 1.22. This result has a large uncertainty both because of the statistical uncertainty of the experimental values on which it is based and because the calculation of the distribution coefficient in seawater is sensitively dependent on the values assumed for the ionic activity coefficients, which have not been measured directly.

The values indicated in Table 1 for the distribution coefficient of molecular hydrogen sulfide between nitrogen and sewage effluent are highly anomalous. The very large numbers calculated for the coefficient probably mean that only a small fraction of the total sulfide determined by the methylene blue procedure is free to participate in the ionic equilibrium. In calibrations of the sulfide ion-selective electrode in the same sewage effluent medium, anomalously low values of sulfide ion activity have been observed at pH less than 6. Because of these effects in sewage effluent and the probable dependence of P_D upon ionic strength of the sample, gas sparging does not provide an independent and reliable check of the gas-sensing electrode in media of uncertain composition.

SECTION V

GAS-SENSING ELECTRODE

PRINCIPLES

The use of a potentiometric sensor for the activity of dissolved gases dates from the carbon dioxide electrode (10,11), which has found biological and medical applications. Since then, ammonia (12) and, more recently, sulfur dioxide and NO_X (13) electrodes have become commercially available. These sensors are based on the principle discussed in detail previously (13) of allowing the dissolved molecular species to diffuse through a permselective membrane that is impermeable to ionic species. In the interior of the probe the molecules react with the filling solution to form characteristic ions that are sensed conventionally. For example, carbon dioxide and ammonia each change the pH of the filling solution and are detected by a conventional glass electrode inside the body of the probe. Selectivity is obtained by choice of the filling solution and of the permselective membrane. Recently Ruzicka and Hansen (14) have described a gas-sensing electrode in which an air gap replaces the diffusion membrane. Surface tension presumably holds a film of electrolyte on the surface of the sensing electrode.

For the measurement of hydrogen sulfide, a silver sulfide solid state probe for detecting product sulfide ions in the filling solution is a logical choice. Two electrodes based on the ammonia-sensing electrode design, were made on special order by Orion Research, Inc. The contractor developed the filling solution, suggested the use of lanthanum fluoride as an inner reference electrode, and furnished two types of membranes used in the commercial ammonia and sulfur dioxide probes.

The relation between the activities of sulfide ion and molecular hydrogen sulfide is pH-dependent and requires that the filling solution be well buffered with respect to pH. The use of a lanthanum fluoride reference electrode, which is selective for fluoride ion, eliminates any direct response to other acid gases, particularly carbon dioxide, that might also diffuse through the membrane. One of the porous diffusion membranes was made of Teflon^R and the other, polyvinylchloride. The hydrophobic character of the plastics prevents penetration either by the inner filling solution or the external test solution. Consequently, the actual diffusion barrier consists of air trapped in the pores, and the membranes should be almost ideally osmotic.

The combination of features made a probe that was expected to be almost perfectly selective for molecular hydrogen sulfide. The specifications for the filling solution are given in Table 2.

Although the gas-sensing electrode is expected to be highly specific for hydrogen sulfide, several aspects of its performance were recognized as being potentially limiting:

- Hydrogen sulfide and its ionic products are readily subject to oxidation by air (5). Ascorbic acid was included in the filling solution to guard against such reactions. Similar precautions may be needed in handling standard and test sclutions.

- As mentioned above, the filling solution must be buffered with respect to pH to maintain a constant fraction of the total sulfur in contact with the sensing crystal as the sulfide ionic species. Further study may be needed to determine the optimum pH and the extent of buffering required. A filling solution with a high pH would tend to convert substantially all the diffusing hydrogen sulfide to sulfide ions, thereby providing the lowest detection limit, but the response on going from higher to lower levels of H_2S in the test solution might be expected to be very slow because of the very low concentration of molecular H_2S (at high pH) inside the probe, available for diffusion. At equilibrium, the activity of molecular H_2S must be the same on both sides of the membrane; the quantity that must diffuse across the membrane, in either direction, when changes are made in the external solution, must therefore be much greater when the filling solution is at higher pH.

- Since the diffusion membrane is nearly ideal osmotically, significant amounts of solvent (water vapor) may be transferred across it if the sample and filling solutions differ appreciably in osmotic strength. The desirability of pH buffering and protection against oxidation led to a recommended filling solution (Table 2) that had an ionic strength of 1.2. This is much greater than the value for most samples of interest and would promote the transfer of water to the interior of the probe.

- The membrane will probably have a finite life, possibly limited by plugging, either by solid debris in the samples or by Ag_2S from the probe electrode.

Table 2. MANUFACTURER'S RECOMMENDED ELECTRODE FILLING SOLUTION

0.2 M	Citric acid
0.1 M	Asorbic acid
0.001 M	Sodium fluoride
pH 6.0	

Ionic strength 1.3

Osmolality, 0.9, approx.

ELECTRODE CONSTRUCTION

The construction of gas-sensing electrodes has also been described elsewhere in considerable detail (13). The elements are shown schematically in Figure 2. The most critical feature is the close proximity of the gas-permeable membrane to the sensing electrode. The volume of filling solution in the liquid film between these elements must be as small as possible to provide a reasonable response rate since concentration changes are effected by diffusion. The filling solution also provides an essential electrical pathway between the sensing and reference electrodes. The latter can be located at some distance from the sensing element since mixing is not critical and the ionic concentration (F^-) to which the reference electrode responds is virtually constant.

TEST METHODS

Tests and calibrations were made at room temperature (22 - 25° C), under nitrogen in closed systems to minimize oxidation of the sulfide. Two basic procedures were used:

- measured additions of a stock solution of sodium sulfide to a constant pH test solution, and
- additions of acid or alkali to vary the pH of a solution with a relatively high and constant concentration of total sulfide.

The test vessel was a 100-ml, round-bottom, multinecked flask, with magnetic stirring bar, nitrogen bleed (adjustable either above or below the solution surface), one or two gas-sensing electrodes, glass electrode, double-junction reference electrode with a nitrate filling solution (Orion Model 90-02-00) and, usually, a sulfide ion-selective electrode (Orion Model 94-16). Potentials were recorded with a Leeds & Northrup Model 7421 Digital pH Meter. The glass electrode was calibrated in buffers at pH 6.87 and 7.42, using the double-junction reference. The meter was then standardized on zero millivolts and millivolt readings were taken for the two buffers. During a run all electrode potentials were recorded in millivolts and the glass electrode results were converted to pH. In some runs, the response of the gas-sensing electrode was recorded on the X-Y chart recorder of a Princeton Applied Research Model 170 Electrochemistry System. The output of the pH meter, connected to the hydrogen sulfide electrode, was applied to the external X-axis input of the recorder. At the same time, the glass and reference electrodes were plugged into

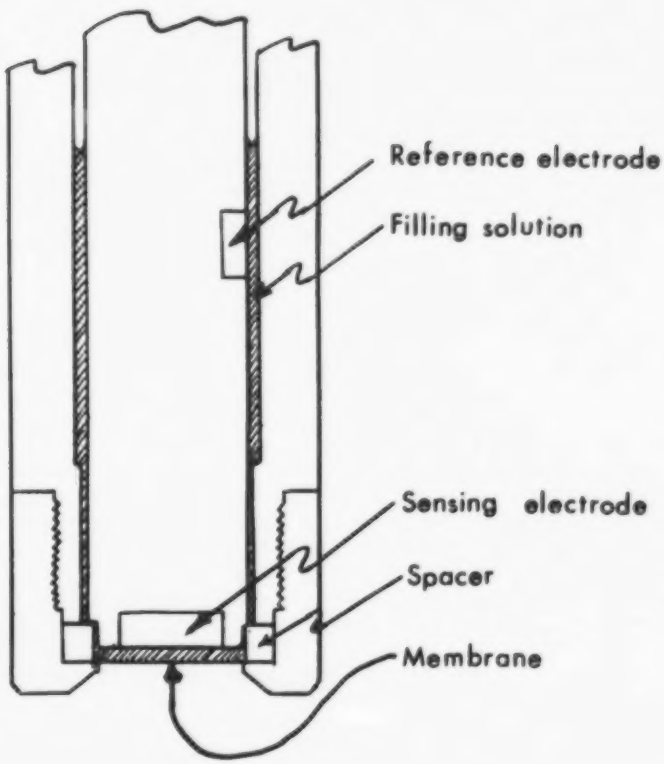

FIGURE 2. Electrode Construction

the jacks of the Model 170, which recorded pH directly on the Y-axis. For rate-of-response curves a ramp voltage was applied to the dummy cell of the Model 170 to provide a vertical Time Scale axis.

Stock sodium sulfide solutions were calibrated daily iodometrically, using As_2O_3 as the primary standard. The concentration of total sulfide was calculated from the volumes of test solution and added stock solution, making allowance for dilution by further additions of acid or base, as appropriate. The sodium sulfide solutions were added from 5- to 10-µl Grunbaum pipets or from a 1-ml Mohr pipet calibrated in 0.01 ml. For the various solutions, pH_2S was calculated from pH and total sulfide by equations 1 and 2.

RESULTS

The manufacturers indicated that the hydrogen sulfide electrodes should give a Nernstian response (30 mV per decade at 25° C) between pH_2S 1 and 8 (15). Subsequently, they have published a response curve (13) indicating a break in the curve about pH_2S 7.5. The response approaches a constant millivolt output at pH_2S 8.

In my tests of the electrodes I almost invariably found a break between pH_2S 6 and 7. Instead of approaching a constant output, the voltage increased sharply (became less negative), often 100-300 mV per decade, and did not reach a constant value even at pH_2S 9. Because of this unexpected and anomalous response the major evaluation effort was directed toward finding the source of the anomaly and defining the range of reliable operating conditions. The former objective was not reached and many experiments at low levels were poorly reproducible.

Figures 3, 4, 5, and 9, showing manual plots of potential (millivolts) *vs.* pH_2S, are presented with an unconventional ordering of scales to provide a direct comparison with tracings of the X-Y recorder (Figures 6, 7, 8, and 11).

Table 3. ELECTRODE DATA FOR FIGURES 3-10

Fig.	Electrode	Membrane	Filling Solution	Test Solution
3a	B	Silicone (Radiometer)	Citric acid, pH 6.0	Citric acid
3b	A	PVC(Orion,SO_2)reused	" " " "	1 M Potassium chloride
4a	B	" " " "	Tris, pH 7.0	Deionized water
4b	A	Teflon (Chemplast) used once	Tris, pH 7.8	Seawater
4c	B	PVC(Orion,SO_2)10 days	" " "	"
5a	B	PVC-used after 3b	Phosphate, resin-treated	Phosphate
5b	A	" " " "	" "	"
6, 9a	B	Teflon (Chemplast)	Tris, pH 7.0	Tris
7, 9b	B	PVC(Orion,SO_2)	" " "	"
8, 9c	B	Teflon(Orion,NH_3)	" " "	"
10	B	Silicone (GE)	" " "	"
(gas)	B	PVC(Orion,SO_2)	" " "	Deionized water (sparge)

Table 4. LINEAR CALIBRATIONS OF HYDROGEN SULFIDE ELECTRODE

Fig.	Range pH_2S	Slope mV/decade	Rel. Std. Dev. of Slope (%)	No. of points	Std. Dev. (pH_2S)
3a	2.7 - 4.6	30.7	0.7 %	7	0.03
3b	4.2 - 7.1	36.7	.7	7	.05
4a	4.4 - 7.6	40.5	1.2	11	.15
4b	3.4 - 5.6	31.3	2.7	6	.11
4c	3.4 - 4.9	16.5	1.3	5	.03
5a	3.5 - 5.2	33.7	1.6	8	.08
5b	3.9 - 7.3	30.8	1.0	7	.08
9a	3.3 - 6.1	28.5	2.0	8	.13
9b	4.3 - 5.8	26.9	1.2	16	.08
9c	4.3 - 5.8	27.5	0.6	8	.02
(gas)	4.1 - 5.7	35.6	1.5	13	.28

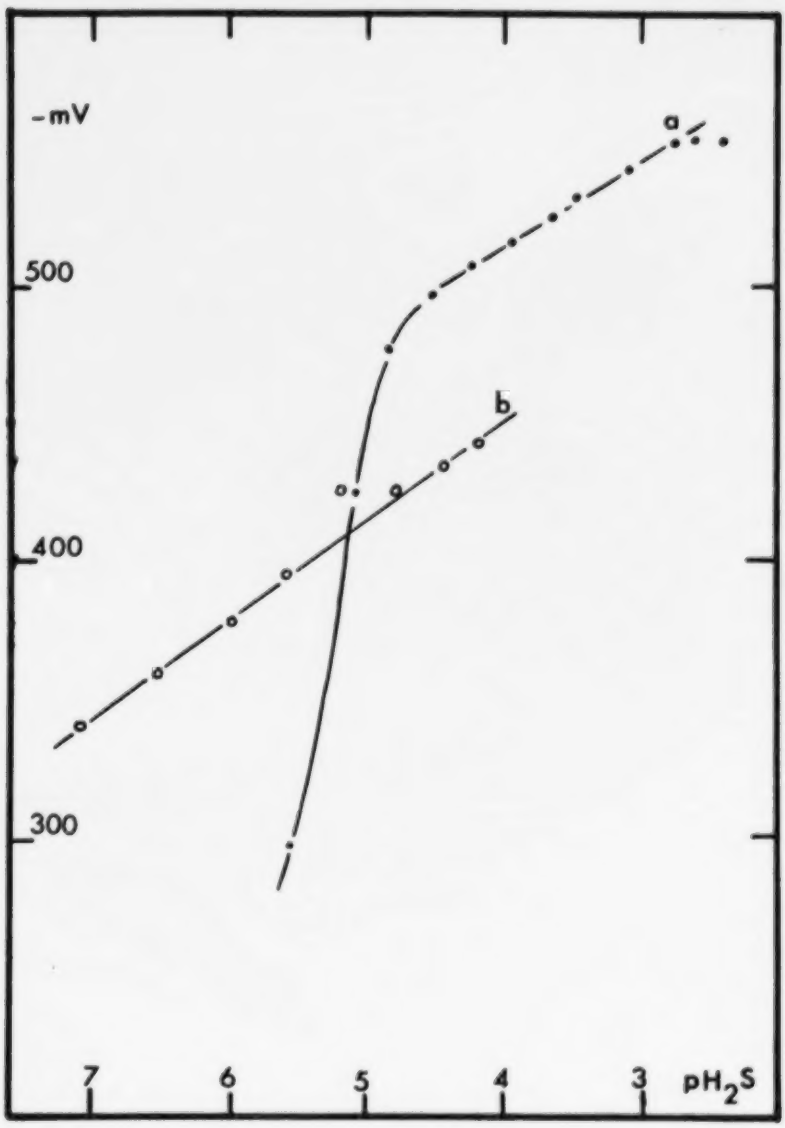

FIGURE 3. Response Curves -- Citric Acid Filling Solution, pH 6

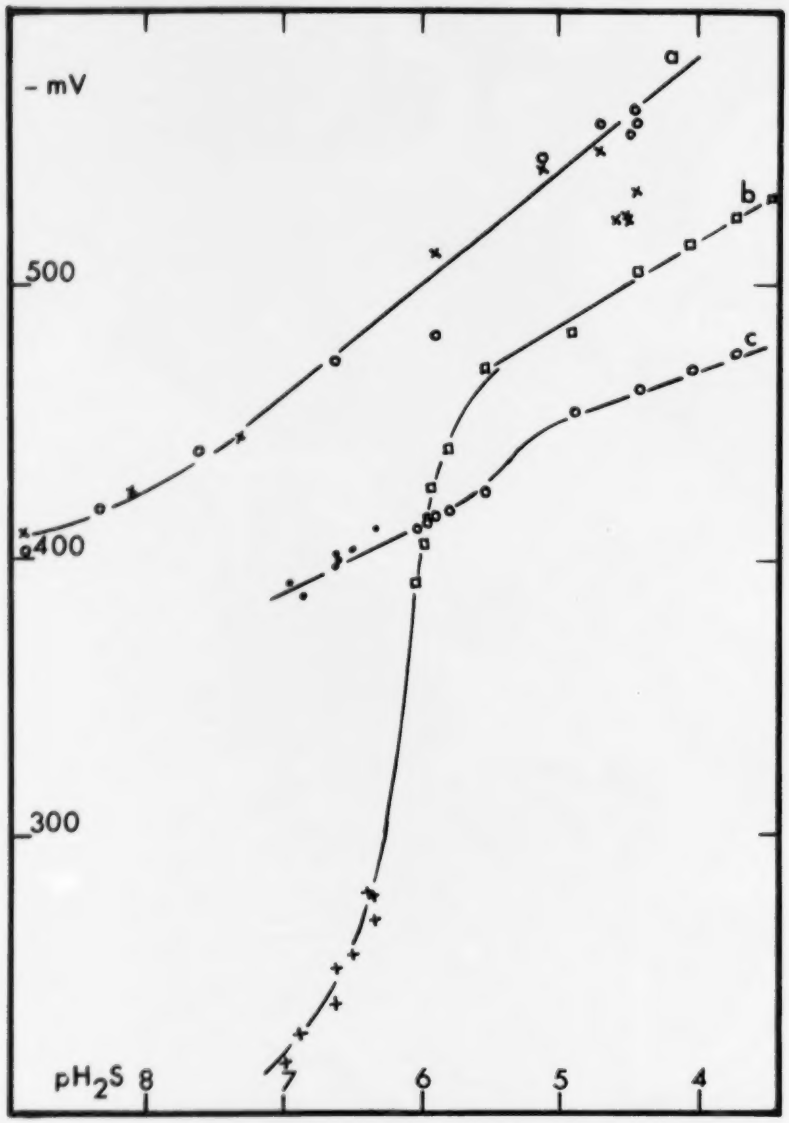

FIGURE 4. Response Curves -- Tris Buffer Filling Solution

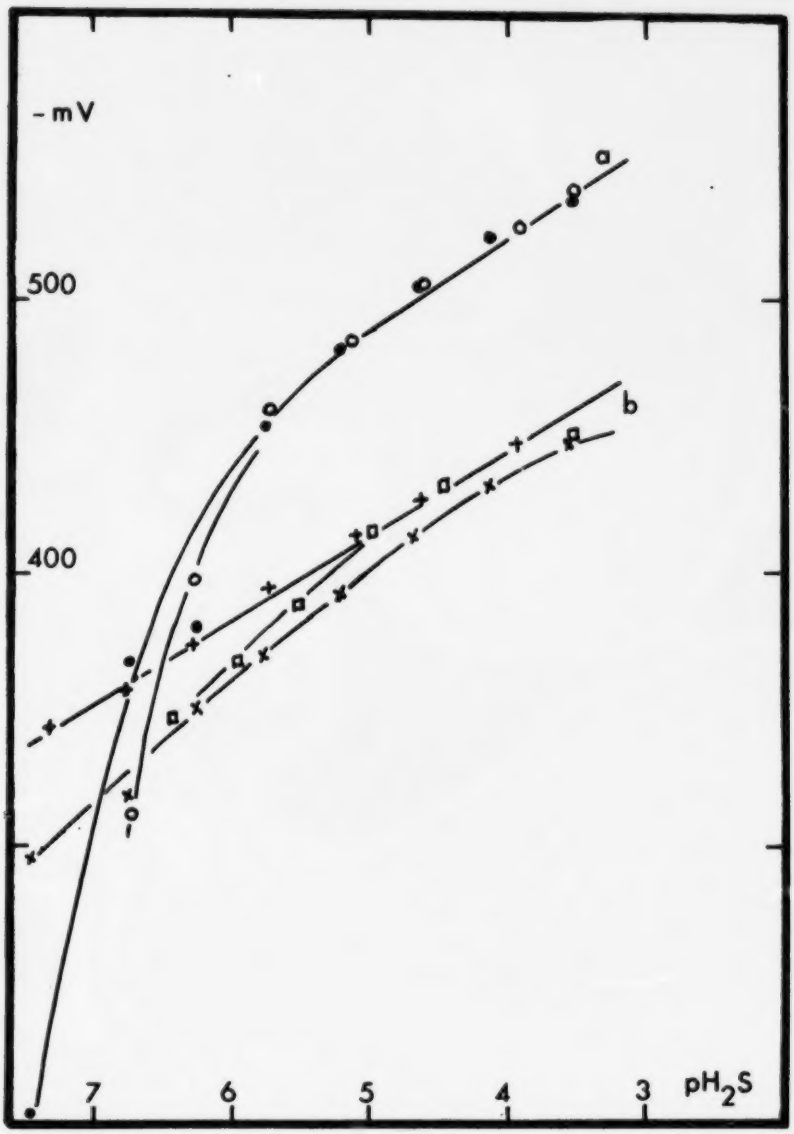

FIGURE 5. Response Curves -- Phosphate Buffer Filling Solution

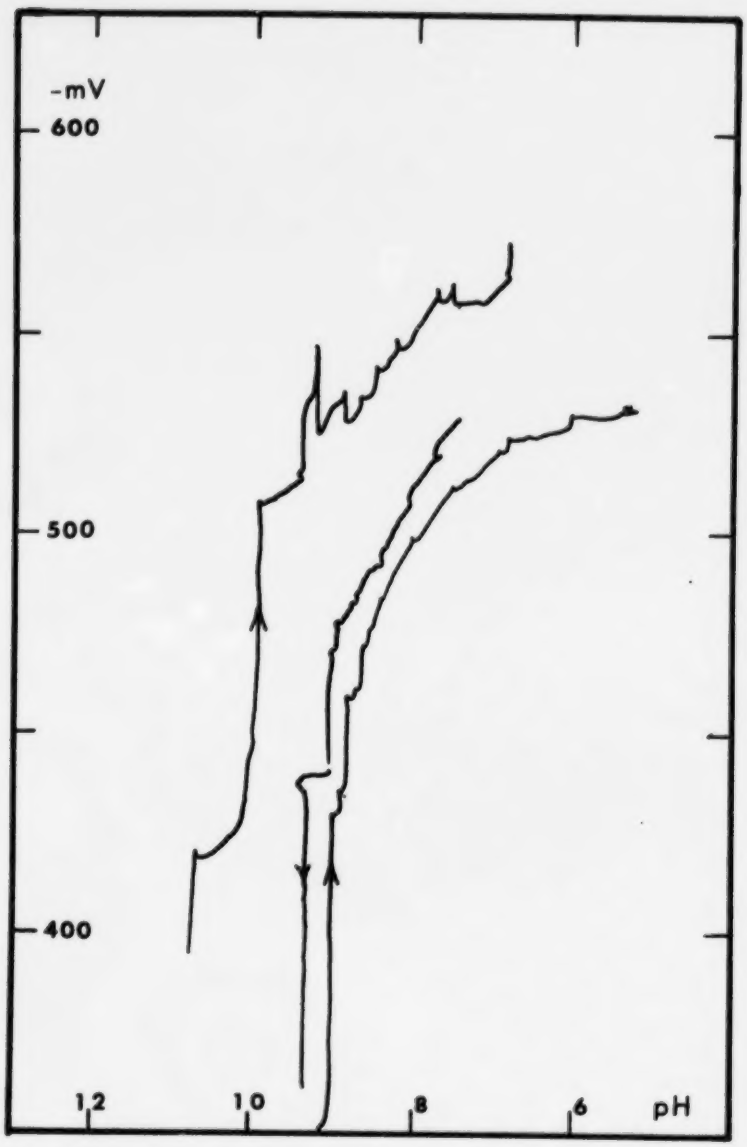

FIGURE 6. Chart Recording -- Chemplast PTFE Membrane

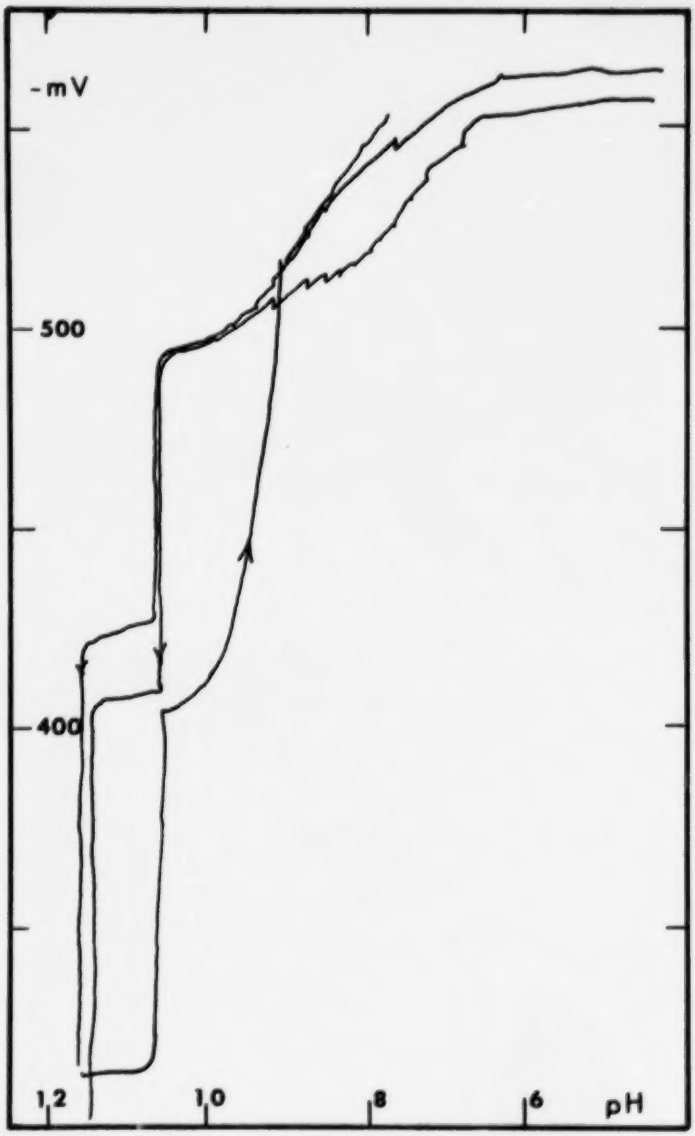

FIGURE 7. Chart Recording -- Orion PVC Membrane

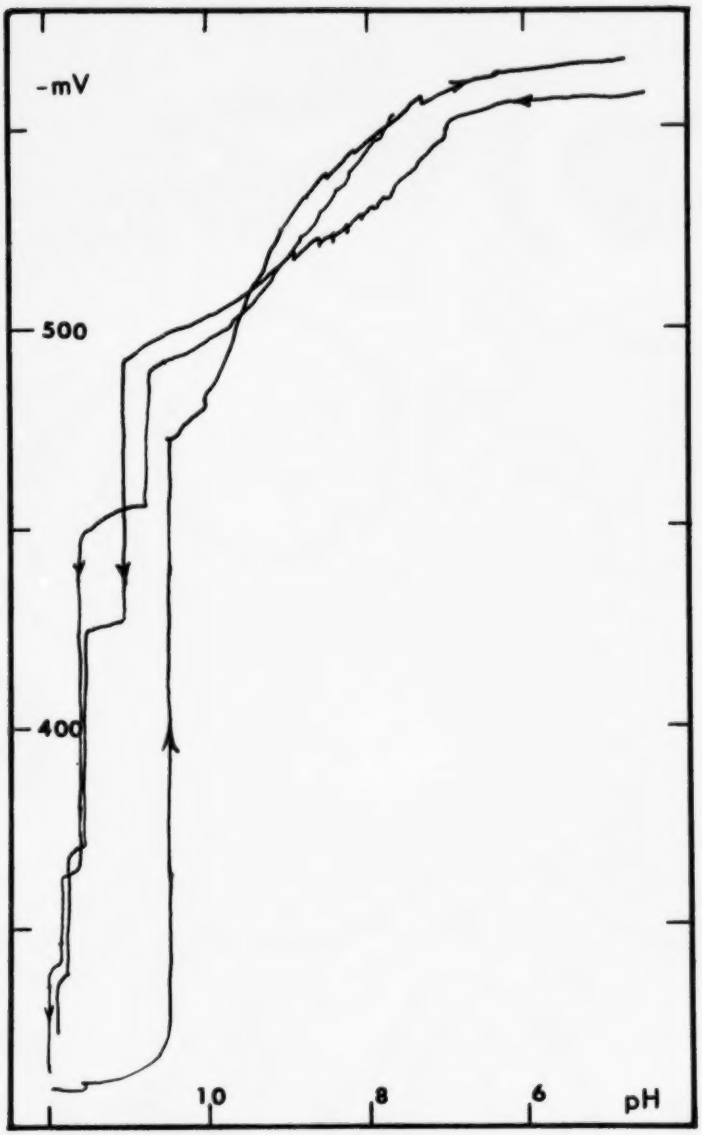

FIGURE 8. Chart Recording -- Orion Teflon Membrane

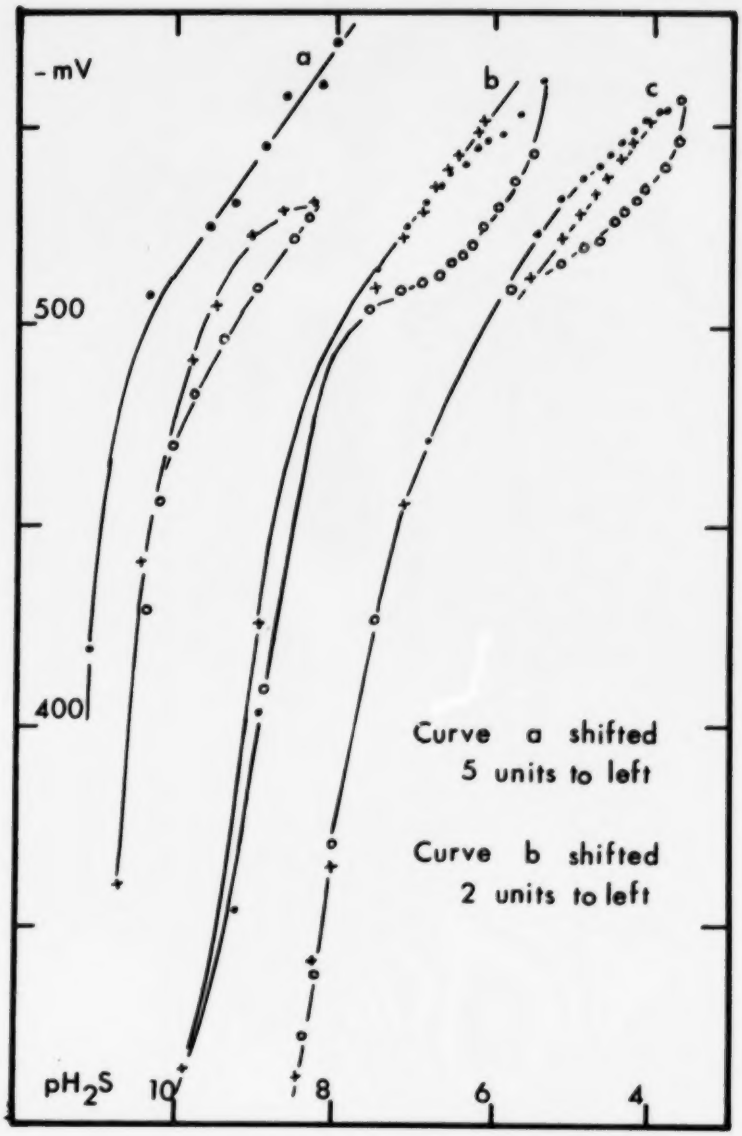

FIGURE 9. Calculated mV *vs.* pH_2S for Figures 6, 7, and 8

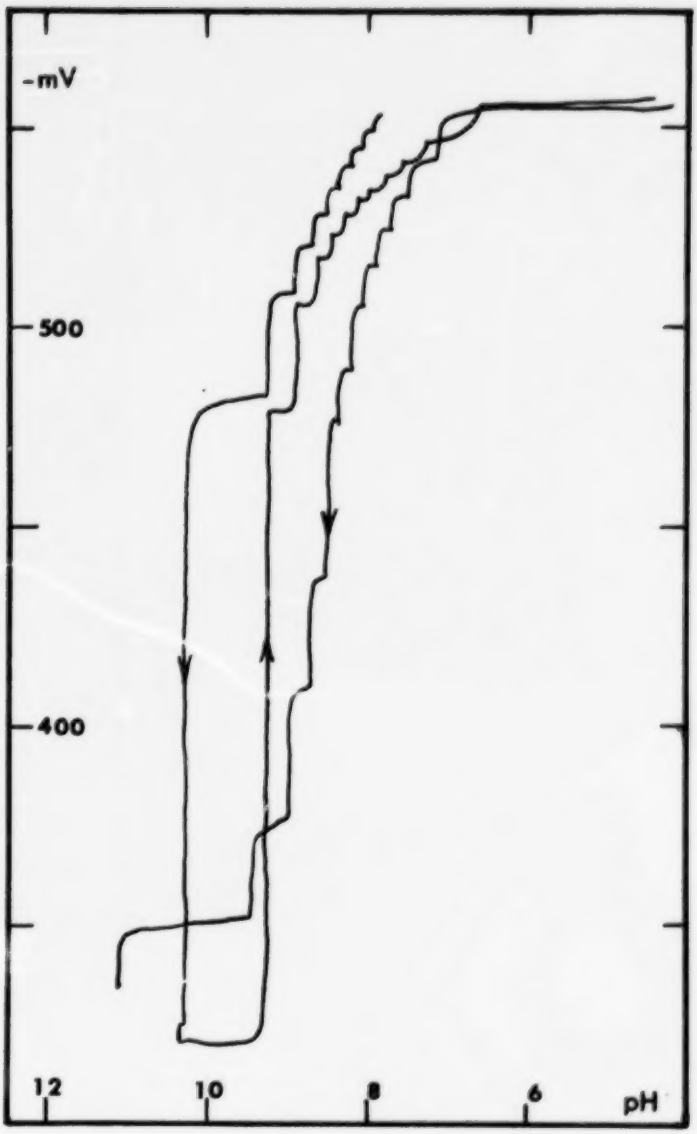

FIGURE 10. Chart Recording -- GE Silicone Membrane

Experimental Factors

Filling Solution--

The principal function of the filling solution, as indicated above, is to provide a constant pH medium for the ionization of hydrogen sulfide so that the free sulfide ions detected by the sensing electrode will bear a fixed relation to the molecular species. Lower limits of detection, in the presence of sufficient total sulfide, have been reported as 10^{-19} M (16) and 10^{-20} M (17) free sulfide ion. At pH less than 8, substantially all the sulfide is in the molecular form, so that the practical detection limit for H_2S may be the same as for total sulfide. This limit was given as 10^{-6} M, provided ascorbic acid was used to prevent oxidation of the sulfide (18).

Examples of the response with the Orion citric acid filling solution at pH 6 are shown in curves a and b of Figure 3. The latter had one of the longest ranges of linear response that was found, although one outlier point was observed. The slope of curve b (36.7 mV/decade - Table 4), however, is considerably greater than the theoretical Nernstian value of 30 mV/decade.

A filling solution with the following composition was also prepared to provide a medium with a higher pH and also a smaller ionic strength:

0.1 M Tris(hydroxymethyl)aminomethane

0.1 M Ascorbic acid

0.001 M Sodium fluoride

This solution was adjusted to pH 7.0 in Figures 4a, 6, 7, 8, and 10, and to pH 7.8 in Figures 4, b and c. Figure 4a also showed a long linear range of response, but with considerable scatter, and also showed a greater than Nernstian slope (40.5 mV/decade). There was no clear difference in suitability of the two filling solutions.

Ionic Strength of the Sample--

Because the electrode membrane should function nearly ideally as an osmotic membrane, most tests were made in solutions having the same composition as the respective electrode filling solution (except for the addition of sulfide and, usually, omission of sodium fluoride). This was the case in Runs 3a, 6, 7, 8, and 10. To compare the response in various media Run 3b was made in 1 M potassium chloride (approximately the same ionic strength as the citric acid filling solution), Runs 4b and 4c in seawater

(ionic strength greater than that of the tris filling solution), and Run 4a in deionized water. Run 4a corresponded closest to the behavior described by the manufacturer (10, 11), suggesting that osmotic transport of water in the direction of hydrogen sulfide diffusion might have aided the response. However, if sufficient solvent were transported to alter significantly the concentration at the silver sulfide crystal surface, a less-than-Nernstian response would be expected in low ionic-strength test media and high response slope in media of high ionic strength. On the contrary, the distilled water run (4a) had a large slope and one of the seawater runs (4c) had the smallest slope. In all calculations of pH_2S, the activity coefficient of hydrogen sulfide was taken as unity, regardless of the ionic strength of the medium. As mentioned in the discussion of gas sparging, this assumption probably does not contribute more than 0.3 log unit error in pH_2S.

Diffusion Membranes--
The electrodes were supplied with two commercial types of diffusion membranes: a polyvinylchloride (PVC) membrane (Orion Cat. 95-64-04) and a Teflon^R membrane (Orion Cat. 95-10-04). In addition, membranes were cut from TFE medium filter membranes (Chemplast 75-M), paper-backed silicone rubber (Radiometer MEM-213), and General Electric dimethyl silicone film. The silicone films are of interest because they transport hydrogen sulfide by condensed-phase, rather than gaseous, diffusion. The silicone films were cemented across the end of the electrode holder with Dow Corning silicone adhesive.

The membranes used for the various runs represented in the charts are summarized in Table 3. Two major qualitative observations were made: the silicone films reached steady-state response more slowly than the gaseous diffusion membranes, and the high-permeability membranes (TFE filter and PVC) occasionally became flooded with liquid. When a continuous liquid pathway was established through the membrane the electrode responded to sulfide ion rather than to hydrogen sulfide species.

The useful life of each membrane was not determined since the major emphasis was on optimizing conditions for the lowest detection limit. Most runs were made with fresh membranes. Run 4c, however, was recorded with a PVC membrane that had been in place for ten days and used for four prior runs. Except for the flooding, alluded to above, there were no indications of membrane failure.

Rate of Response--
The rate at which the electrode responded to abrupt changes in concentration of hydrogen sulfide was recorded for various levels within the range studied above. Tracings of the recordings are shown in Figure 11. Curves a - e were recorded immediately following the run shown in Figure 7, in which an Orion PVC membrane was used; curves f and g were recorded after the run shown in Figure 8, using an Orion Teflon membrane; and curves h - k were obtained following the run shown in Figure 10, using a methyl silicone film. In all cases, the change in hydrogen sulfide concentration was made by pH adjustment between the values shown in Table 5.

As expected, the response was qualitatively faster in the more concentrated solutions, reaching steady potentials in about a minute (curves c and i). Empirical fitting of Equation 3 to these curves was attempted as a means of obtaining improved estimates of the final potential, E_f, and a measure of the diffusion constant, K, for the various membranes.

$$E = E_f + B \ln [1 - A \exp (-Kt)] \qquad (3)$$

Equation 3 was derived on the basis of a Nernstian-type of response of potential, E, to the concentration of sulfide ion reaching the sensor surface at time, t, by linear diffusion. Constant B is the Nernst factor and A is the ratio of the initial concentration difference providing the diffusion potential, to the final (sample) concentration at the electrode. Equation 3, above, is equivalent to equation 8 of reference 13, with $1/K = (lm/Dk)[1 + (dC_B/dC)]$ of the reference.

Several methods of non-linear least-squares fitting of Equation 3 to the data for curve b of Figure 11 showed that the four constants could not be evaluated with any certainty. Within the 2-mV estimated precision of the measured values of E a very wide range of parameters gave an acceptable fit, as shown in Table 6. The Simplex (19) and Pletcher-Powell (20) procedures are systematic techniques for minimizing the variance of fit, but each was converging very slowly when the calculations were stopped. The best fit that was found was by a rather lucky guess in a trial-and-error approach but there is no assurance that it was the least-squares "best" fit. The expected values of the constants were obtained as follows: The curve was visually extrapolated to long times to give E_f; B is the theoretical Nernstian value in millivolts per unit natural logarithm of

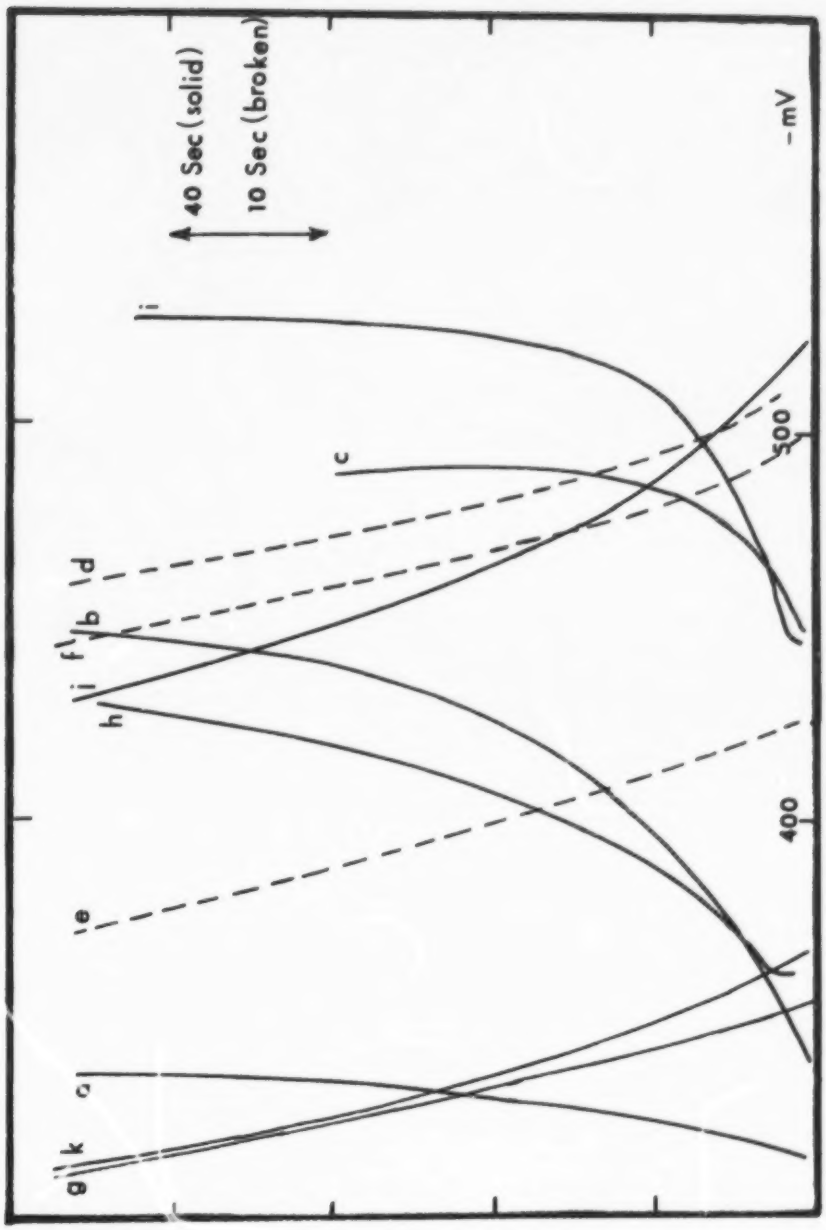

FIGURE 11. Electrode Response Rate Curves

Table 5. CONDITIONS FOR ELECTRODE RATE CURVES SHOWN IN FIGURE 11

Curve	ΔpH	ΔpH_2S
	Following calibration shown in Figure 7	
a	11.5 - 9.4	8.41 - 6.37
b	9.4 - 8.8	6.37 - 5.82
c	8.8 - 8.5	5.82 - 5.49
d	<8.5 - 9.3	5.49 - 6.26
e	9.3 -11.1	6.26 - 7.99
	Following calibration shown in Figure 8	
f	7.8 - 11.0	4.86 - 7.97
g	11.0 - 11.7	7.97 - 8.70
	Following calibration shown in Figure 10	
h	>11.1 - 5.9	8.04 - 3.85
i	5.9 - 2.7	3.85 - 3.80
j	2.7 - 7.3	3.80 - 4.42
k	7.3 - 7.8	4.42 - 4.82

Table 6. PARAMETERS OF EQUATION 3 OBTAINED BY FITTING TO DATA FOR CURVE 11b

Procedure	Constants				Variance of Fit (mV^2)
	$-E_f$	B	A	k	
Simplex	500.7	33.94	1.0047	0.001371	3.33
Fletcher-Powell	498.6	35.49	1.0025	.001616	3.32
Trial & Error	467.0	67.1	0.859	.0072	3.14
Interpolation	457.8	120.3	.6415	.01208	1.037
Trial & Error	453.6	168.6	.5	.0143	0.229
Expected Value	480	13	0.715	40	700

concentration; A was calculated from the estimated initial and final concentrations of H_2S (Table 5); and K was very crudely estimated for free-air diffusion of gaseous H_2S by equation 4.

$$K = DA/P_DVT \qquad (4)$$

In equation 4, D is the diffusion coefficient (0.1), A the area (0.1 cm^2), T, thickness (0.1 cm), V, liquid volume ($1x10^{-3}$ cm^3), and P_D is the distribution coefficient measured in the sparge runs (2.5). It is clear, that the curve-fitting approach did not give useful estimates of the physical parameters, although the very large discrepancy in K may indicate that liquid diffusion is actually the rate-limiting process.

Gaseous Sampling--
Because the electrode is truly "gas-sensing" it should be capable of measuring hydrogen sulfide in air, or other gases, as well as in solution. To test its gas analysis capabilities, the electrode was placed at the top of the sparge column (Figure 1) containing initially 1.91×10^{-4} M sodium sulfide in deionized water. In two runs with the same electrode the solution was sparged with 1.5 to 8 l of nitrogen at two pH levels (6.5 and 5.4). The results are not plotted but are summarized in the final lines of Tables 3 and 4. The data cover a relatively narrow range of pH_2S (4.1 to 5.7) and show considerable scatter but generally show a linear response (potential vs. log concentration) with a somewhat greater than Nernstian slope.

MECHANISM OF THE ANOMALOUS RESPONSE

As indicated above, a large part of the effort was directed toward understanding and correcting the extremely non-Nernstian response usually observed at values of pH_2S greater than 5 or 6. The usual low-concentration limitation of ion-selective electrodes is a lack of response, or near-zero slope, rather than the great increase in slope observed in this work. Several possible causes of this phenomenon were considered.

Crystal Defects

In a recent paper, Morf, Kahr, and Simon (21) reported similar behavior by Ag_2S and AgI electrodes. This is the only independent confirmation of the sharp break in potential response that the writer has found. They interpreted the results in terms of crystal surface defects that strongly adsorbed free silver ions. Their data were explained by an assumed defect activity equivalent to 3×10^{-6} M free silver ions in solution. In the present study, the corresponding defect activity was approximately 10^{-14} M, which was the activity of free sulfide ions at the potential break. A consequence of the theory, which was not tested, is that the detection limit for hydrogen sulfide might be lowered by increasing the pH of the filling solution to pH 9 or greater, thus increasing the relative concentration of sulfide ion. That modification would be expected to slow the response time of the electrode at low concentrations of hydrogen sulfide. The theory of Simon and co-workers (21) does not seem to account for the well established response of the silver sulfide electrode to extremely low activities of free sulfide ion (17) or silver ion (22) in the presence of at least 10^{-4} M total sulfide or complexed silver.

Heavy Metal Poisoning

The resemblance of the electrode response to potentiometric titration curves suggested that the first traces of hydrogen sulfide to diffuse through the semi-permeable membrane were precipitated by heavy metal contaminants in the filling solution. That mechanism would not account, however, for the same sort of response on going from higher to lower concentrations of hydrogen sulfide. Baumann (23) lowered the detection limit of the electrode for sulfide ions by a factor of three by ion-exchange pretreatment of her buffers. For the runs shown in Figure 5 the phosphate-buffered filling solution was pre-treated by Chelex ion exchange resin. In one case (curve b) the response is more nearly linear but could not be reproduced and the difference between the runs is unaccountable.

Carrier Mobility

The possibility was considered that the response of the electrode might be limited by the concentration or mobility of charge carriers in the silver sulfide crystal. The resistance of the silver sulfide electrode in combination

with various reference electrodes (lanthanum fluoride, Orion double junction, silver-silver chloride) was measured by the technique of Eckfeldt and Perley (24). The lowest apparent resistance was 11 MΩ. This high dc resistance tends to confirm the conclusion (25), based on ac impedance measurements, that the silver sulfide electrode acquires a potential by capacitive coupling with the solution rather than by ion exchange.

Surface Condition of the Crystal

By rigorously controlled preconditioning of a copper sulfide electrode, copper ions were determined kinetically at concentrations well below the equilibrium detection limit (26). A similar approach may be the key to lower detection limits with the silver sulfide electrode. In this work the electrode commonly became dull and dark colored after a few runs. This did not necessarily affect the response, but when erratic results were obtained at relatively high levels of hydrogen sulfide the crystal was re-polished by rubbing with a few milligrams of Cab-O-Sil silica on a dry, hard filter paper. Some improvement in response was noted.

CALIBRATION

Despite the anomalous response of the gas-sensing electrode at very low levels of hydrogen sulfide the response generally was Nernstian for pH_2S less than 5.5, (i.e., H_2S activity greater than 0.1 mg/l). Since this lower limit is close to the organoleptic detection limit (27), the electrode may well have a significant application in the examination of anoxic or polluted natural water or wastewater.

For the practical calibration of the electrode, stock sodium sulfide solution was added to commercial pH buffers. Buffers for pH 4.01 (potassium hydrogen phthalate) and pH 9.18 (borax), when made 1×10^{-3} M in sodium sulfide, had pH values of 4.6 and 9.7, respectively. The corresponding calculated values of pH_2S were 3.203 and 6.0. The latter value depended, within 0.08 unit, on the exact pH of the resulting solution, in the six preparations made, while the former was independent of small pH variations (within 0.08 pH unit). Calibrations over a period of three weeks for various filling solutions and membranes gave the following values for the mean slope, $\Delta mV/\Delta pH_2S$: 32.1, 30.9, 15.1, 15.5, 30.6, 48.0, 27.2, 24.3, 151. The last value indicates

that the potential break occurred at a pH_2S less than 6.0 (the higher calibration point) and corresponds to Run a Figure 9. Of the nine values listed above, four are reasonably close to the Nernstian value of 29.6. The calibration slopes of 27.2 and 24.3, above, correspond to Runs b and c, respectively, in Figure 9, which had linear slopes of 26.9 and 27.5 (Table 4).

Calibration standards should correspond to the concentration range for which the electrodes are to be used and the total sulfide concentration, at least in the pH 9.18 buffer, should probably be increased to provide a pH_2S less than 5.5.

SECTION VI

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